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Effect of water activity and glass transition on critical preservation conditions of dried squids**

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A b s t r a c t. Desorption isotherms of dried squids were obtained at different temperatures. Several models were tested to describe the experimental desorption data. The GAB equation gave the best fit over the whole range of water activity and temperature. The glass transition temperature of dried squids was measured using differential scanning calorimetry. The Gordon-Taylor equation was used to model glass transition temperature and moisture content relationship. At a given storage temperature of heat pump-dried squid, the critical water activity/water content can be obtained using the GAB and Gordon-Taylor equations.

K e y w o r d s: water activity, sorption isotherms, glass transition temperature, preservation, dried squids

INTRODUCTION

Dried squid, made by drying after removal of the internal organs, has been highly valued in many parts of the world for its characteristic flavour which develops upon drying. Dried products have long shelf life due to their low water activity which prevents or inhibits fungal and bacterial growth under normal storage conditions, and the drying temperature plays an important role in the quality of the products (Alibas, 2006; Corzo *et al*., 2006). Squid is a fatty fish and its oil contains considerable proportion of highly unsaturated acids (Fu *et al*., 2007). So oxidation in storage can cause serious problems in storage of dried squids.

Water activity (α_w) and glass transition temperature (T_g) provide valuable information on the effects of water content on water availability in foods and on the physical state of food solids. Water activity measures the availability of water for deteriorative changes or microbial growth (Abramovic and Mojca, 2008). The moisture content changes depending on difference between water activity in the material and humidity of the surrounding air (Blahovec, 2007; Domian and Poszytek, 2005). Water sorption isotherms show the relationship between the equilibrium moisture content of foods and the water activity, or the relative water vapour pressure at constant temperatures and pressures (Tymczyszyn and Diaz, 2008).

The glass transition temperature is also a very important physical parameter which serves for the explanation of the physical and chemical behaviour of food systems (Perdomo and Cova, 2008), and it is defined as the temperature at which the material changes from the glassy to the rubbery state for a given heating rate (Tokuyama, 2006). Molecular mobility in the glassy state is extremely slow, due to the high viscosity of the matrix (about 10^{12} Pa s). Thus, T_g, can be taken as a reference parameter to characterize the properties, quality, stability and safety of food systems. The plasticising effect of water on food biopolymers is very small at low water activity values, therefore the T_g associated with the amorphous regions in the sample will be typically high and at room temperature the material may be glassy (Bhandari and Howes, 1999; Delgado and Sun, 2002), with greater water content resulting in decreased glass transition temperatures (Mitrus and Mościcki, 2009).

Safety and spoilage of foods are major concerns of food manufacturers, retailers and consumers. Preservation achieved by dehydration requires data on the thermodynamic properties pertaining to water activity. There have been only limited attempts to establish a link between water activity and glass transition temperature for specific food products (Sablani *et al*., 2007).

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This paper aims to build on this understanding by examining water sorption properties and glass transition temperature data for dried squids.

MATERIALS AND METHODS

Frozen fresh squids were purchased from Wuxi Food Market (Jiangsu, China). The squids were stored in a cold chamber at -18°C and their body water content (after removal of the internal organs) was measured to be 84.57±0.28 (%, w.b.). After cleaning they were dried at a drying air temperature of 60°C and air velocity of 1 m s^{-1} at a relative humidity of 30%. The heat pump oven (made by Shanghai San Ling Insti- tute of Environment and Energy) was used to dry squid, and the differential scanning calorimetry (DSC) equipment was used to detect the glass transition temperature of heat pump dried squids. Reproducibility and uncertainty of data were found to be in the range of 1 and 5%. Sorption isotherms were determined by the gravimetric method (Greenspan, 1997). In this method, about 2 g heat pump-dried samples are placed in open weighing bottles and stored in air-sealed glass jars while maintaining equilibrium relative humidity with saturated salt solutions, giving α_w of 0.01×% RH (relative humidity). Salts normally used are KOH, LiCl, KF, $MgCl_2$, NaBr, NaCl and KNO_3. Relative humidity values for these solutions can be obtained from Greenspan (1977). The jars were placed in a temperature-controlled cabinet maintained at a constant temperature. The temperature of water sorption isotherms presented in the literature varies from 10 to 40°C. Twice per day, the samples were removed and weighed until the mass loss or gain reached ≤0.001 g for two successive weighing. Once equilibrium is reached, the equilibrium moisture content (*EMC*) of the sample was measured gravimetrically by drying in an oven at 105°C for at least 24 h to determine the solid mass in the sample (Sablani *et al*., 2007).

The widely accepted and representative models for sorption isotherms for food were chosen according to Madamba *et al*. (1994):

1) The GAB model is widely accepted mainly due to its accuracy and its validity over a wide range of water activities from 0.1 to 0.9:

$$EMC = \frac{m_0 {}^{\mathrm{bc}} \alpha_w}{(1 - \mathrm{c}\alpha_w)(1 + (\mathrm{b} - 1)\mathrm{c}\alpha_w)}, \quad (1)$$

where: m_0 is the monolayer moisture content (d.b.), b and c are constants.

2) The BET model:

$$EMC = \frac{m_0 {}^{\mathrm{c}} \alpha_w}{(1 - \alpha_w)[(1 + (\mathrm{c} - 1)\alpha_w]}. \quad (2)$$

3) The Smith model:

$$EMC = \mathrm{a} + \mathrm{b} \ln (1 - \alpha_w), \quad (3)$$

where: a is the constant.

The glass transition temperature of squid was determined using a model DSC-7 instrument, Perkin-Elmer, USA. The instrument was calibrated by using indium standard. Sample of 10 mg was placed into the DSC pan (B016-9316), and hermetically sealed. An empty pan was used as reference (air). The sample was first cooled to -80°C at 10 °C min^{-1}, then scanned from -80 to 80 °C at a rate of 10 °C min^{-1} to determine its thermal behaviour. Before scanning samples, a scan of two empty pans under the same test conditions was conducted for obtaining baseline subtraction (Duan *et al*., 2008). In this paper, mid-point temperature is reported as the glass transition temperature (T_g) (Sablani *et al*., 2007).

The Gordon-Taylor model Eq. (4) was used to describe the relationship of water content and glass transition temperature:

$$T_g = \frac{(1 - x_w)T_{gs} + \mathrm{k}x_w T_{gw}}{(1 - x_w) + \mathrm{k}x_w}, \quad (4)$$

where: k is an empirical constant of the Gordon-Taylor equation, and x_w is the water content of squid (w.b.), T_{gw} is a constant (equal -135°C), and T_{gs} is the glass transition temperature of moist solids.

The Gordon-Taylor equation predicts a theoretical complete glass transition curve that approaches the glass transition temperature of the plasticiser as the water fraction increases.

Non-linear regression of the CurveExpert1.3 analysis system was used to evaluate the accuracy of the results. The fitting of models were checked by computation of the coefficient of determination (R^2) and standard error (*S*):

$$R^2 = 1 - \text{Residual SS/Corrected SS}, \quad (5)$$

$$S = \left(\frac{\sum (Y - y)^2}{n - p} \right)^{1/2}, \quad (6)$$

where: *Y* is the experimental data, *y* is the predicted value, *n* is the total number of experimental points, and *p* is the number of the parameters of the models.

RESULTS AND DISCUSSION

The sorption isotherms describe the relationship between water activity (α_w) and the equilibrium moisture content of a given food at a constant temperature. Figure 1 shows the sorption isotherms at different temperatures. It confirms that the equilibrium moisture content leads to rise in water activity; also, at a given water activity, the equilibrium moisture content decreases with increasing temperature.

Three sorption isotherms models were tested to fit the data for water activity and moisture content for the heat pump-dried squids. Table 1 shows the constants of the models obtained using experimental data. Figure 2 shows that the GAB model can best fits the relationship between water activity and moisture content for dried squids. The BET equation is valid only when the water activity is from 0 to 0.5; out of this range, the fit is not very good. The GAB model, which is derived based on the BET model, has also been widely used. Because of its applicability to water activity ranging from 0.1 to 0.9, the GAB equation was chosen to model the sorption isotherms of dried squid.

The change in glass transition temperature with solids content was modelled using the Gordon and Taylor equation. A typical behaviour of solid content and glass transition temperature of dried squids is shown in Fig. 3. The T_g values of dried squids decrease significantly with increase in moisture content. All thermograms for samples with low moisture content show one transition and no formation of ice from water.

The glass transition of pure water was considered as -135°C. The T_{gs} and k values were obtained using non-linear regression. The values of T_{gs} and k were used to estimate T_g at a given water content. The effect of water content on T_g of the heat pump-dried squid followed a non-linear relationship and was described accurately by the following equation:

$$T_g = \frac{88.114 - 310.426 x_w}{1 + 1.523 x_w}. \quad (7)$$

The equation fitted well, with coefficient of determination (R^2) being greater than 0.998 while the standard error was only 3.762. There have been many researches on the

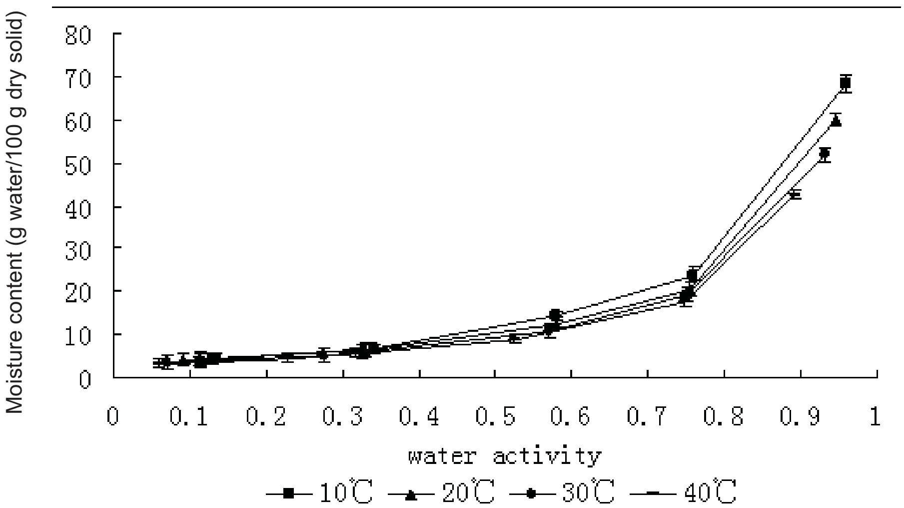

Fig. 1. Sorption isotherms at different temperatures.

T a b l e 1. Comparison of different sorption models when applied to experimental data of dried squid.

Models	Parameters	Temperature (°C)			
		10	20	30	40
BET	m	2.9250	3.3683	3.6337	4.6445
	c	$-1.788\times e^{11}$	$-2.913\times e^{10}$	$7.657\times e^{9}$	19.5568
	R^2	0.9637	0.9837	0.9913	0.9994
	S	7.2755	4.3215	2.5013	0.5356
GAB	m	6.885	5.2446	5.2497	4.0241
	b	12.406	$-2.493\times e^{10}$	15.6839	4.3261
	c	0.9386	0.9450	0.9650	1.0168
	R^2	0.9993	0.9983	0.9993	0.9989
	S	1.1887	1.6257	0.7384	0.8267
Smith	a	-0.5826	-0.9068	-0.6708	-0.3668
	b	-20.6316	-19.5933	-18.1180	-17.3256
	R^2	0.9888	0.9817	0.9801	0.9662
	S	4.0543	4.5781	3.7801	4.0220

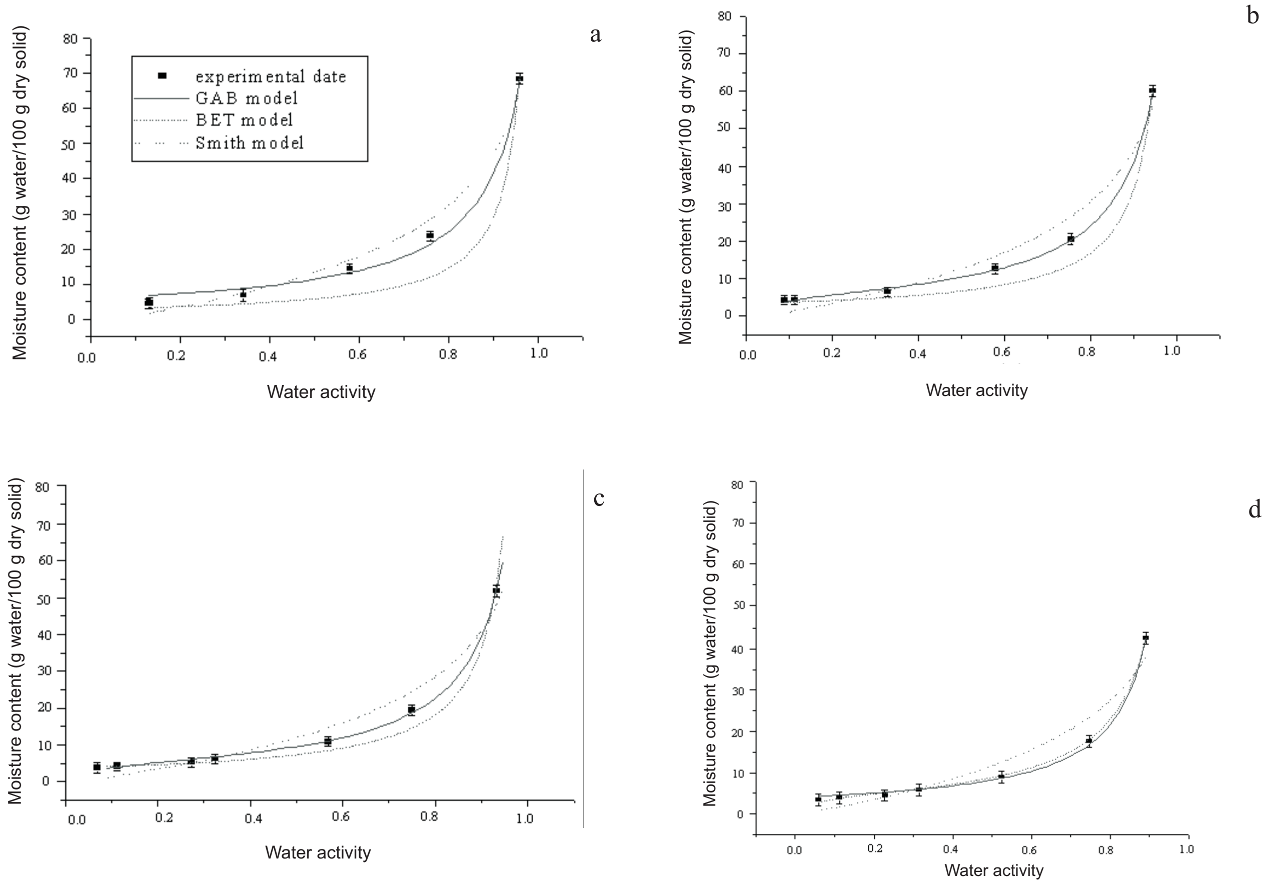

Fig. 2. Experimental data for heat pump-dried squid and predicted sorption isotherms using three model equations at different temperatures: a – 10, b – 20, c – 30, and d – 40°C.

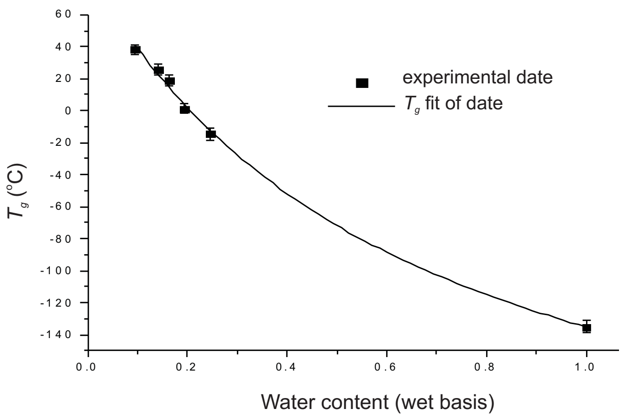

Fig. 3. Variation of glass transition temperature with moisture content for squid.

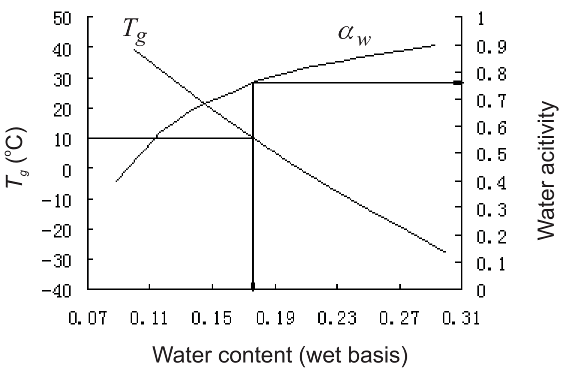

Fig. 4. Relationship between the water activity (α_W), water content and glass transition temperature (T_g) of the heat pump dried squid stored at 10°C.

glass transition temperature of different products (Sablani *et al.*, 2007). The glass transition temperature is not only influenced by the difference of products and water contents, but also greatly influenced by the drying methods applied (Telisa and Sobralb, 2007).

The critical water activity is the α_w value when the preservation temperature of the product equals the glass transition temperature. Molecular diffusion in a glassy state of material is extremely slow. The product can be shelf-stable when stored below glass transition temperature since deterioration due to microbial growth and chemical reaction is greatly retarded. Equation (7) shows that at a given glass transi- tion temperature, the water content of the sample can be calculated, converting the wet basis water content to dry basis following Eq. (7). Then, using the GAB model for the right temperature, critical water activity can be calculated. For example, if the temperature at a warehouse is 10°C, the glass transition temperature of the samples must be 10°C or higher and the water content should be below 17.597% (Eq. (7)); for the temperature and moisture content of dried squid the water activity corresponds to 0.7573 (GAB model). So the best storage conditions of the samples are: x_w = 17.6%, α_w = 0.78 (Fig. 4); for values higher than these the product quality will drop. In other words, when the storage temperature is 10°C, the critical water activity of heat pump-dried squid is 0.76, while the water content of samples is 17.6%:

$$x_w = x_d \,/\, (1+x_d\,), \tag{8}$$

x_d – water content of squid (d.b.).

CONCLUSIONS

1. Experimental results show that the GAB model fits the sorption data for heat pump-dried squid.

2. Critical water activity and preservation conditions for heat pump-dried squid can be obtained by combining measurements of water activity with glass transition temperature.

3. It provides an effective method to relate stability criteria based by the concepts of water activity (α_w) and glass transition phenomenon (T_g).

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